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Fundamental aspects of biomass/coal co-firing

Enrico Biagini, Leonardo Tognotti

Dipartimento di Ingegneria Chimica,
Chimica Industriale e Scienza dei Materiali

Università di Pisa

UNIVERSITÀ DI PISA

INTRODUCTION

Co-combustion: one of the most promising short-term option for the utilisation of secondary fuels.

- Advantages:
  - –reduction in the consumption of fossil fuels
  - –specific advantages exist in the selection of the co-fuel: biomasses may be considered as CO_2 neutral fuels, waste derived fuels may be used as an energy resource instead of lanfilling, low volatile coals can be ignited with minor problems

- Technological problems:
  - –discontinuous availability of biomass materials
  - –low heating values and/or high ash content
  - –ash deposition in the combustion chamber (slagging, etc.)

- Direct utilisation of secondary fuels is actually considered prohibitive.

Projects and materials

- **BioFlam**: Combustion Behaviour of "Clean" Fuels in Power Generation (2000-2002)
- **BioNet**: Development of a New Neural Networks Based Devolatilisation Model for Combustion Calculations of Biomass/Coal Fuels (1998-2000)
- Processi di pirolisi per il recupero di materiali ed energia da rifiuti polimerici e biomasse (MURST 1999-2001)
- **LVC**: Development and Demonstration of a Burner for Low Volatile Coal Combustion (2000-2002)

Biomasses

hazelnut shells
paper sludge
olive residue
pine sawdust
sewage sludge

Coals

Kema 04 (MVB)
coal US (MVB)
coal JW (LVB)
others (LLVB)

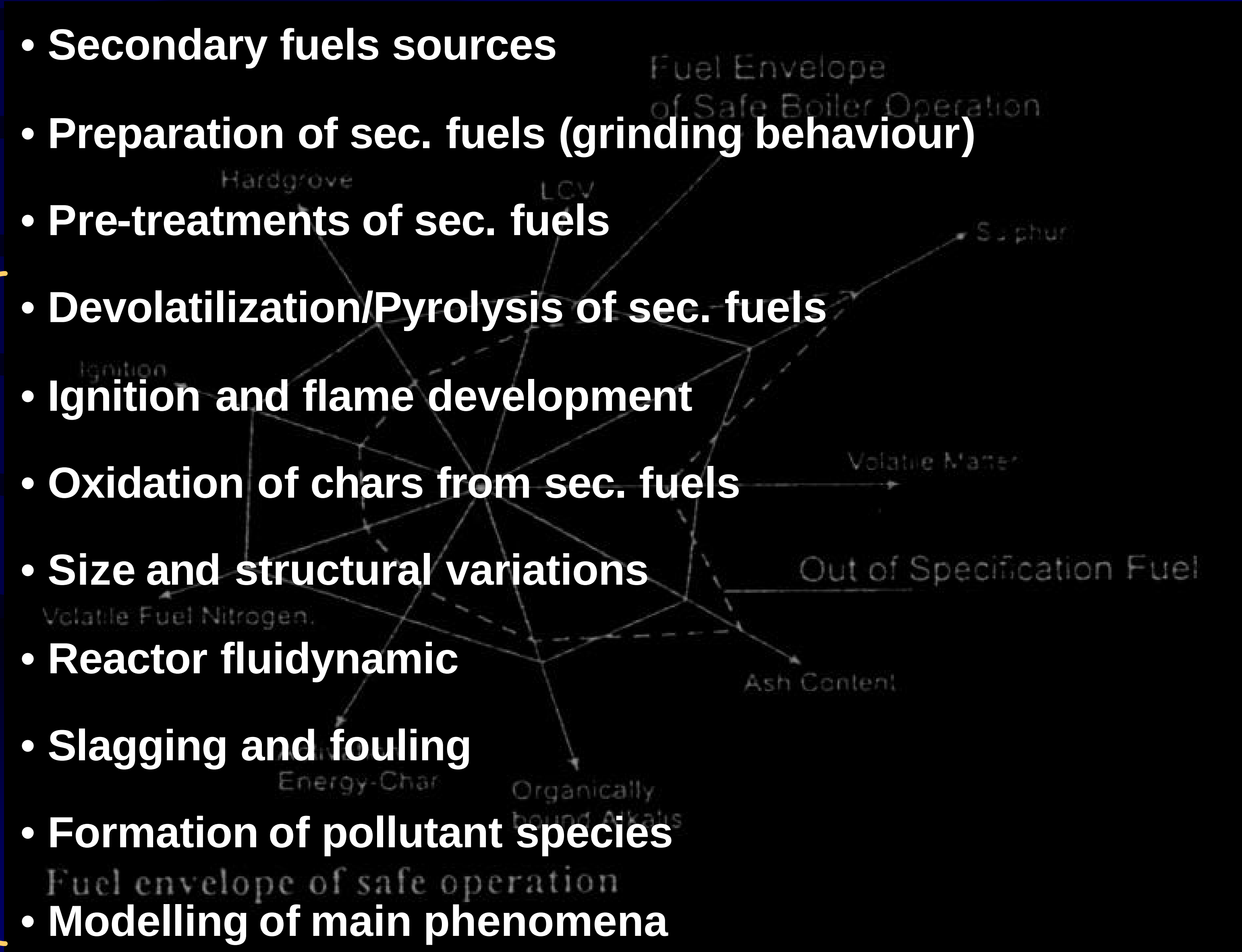
Blends

coal/wood
coal/cacao
coal/sewage sludge
coal/pine sawdust

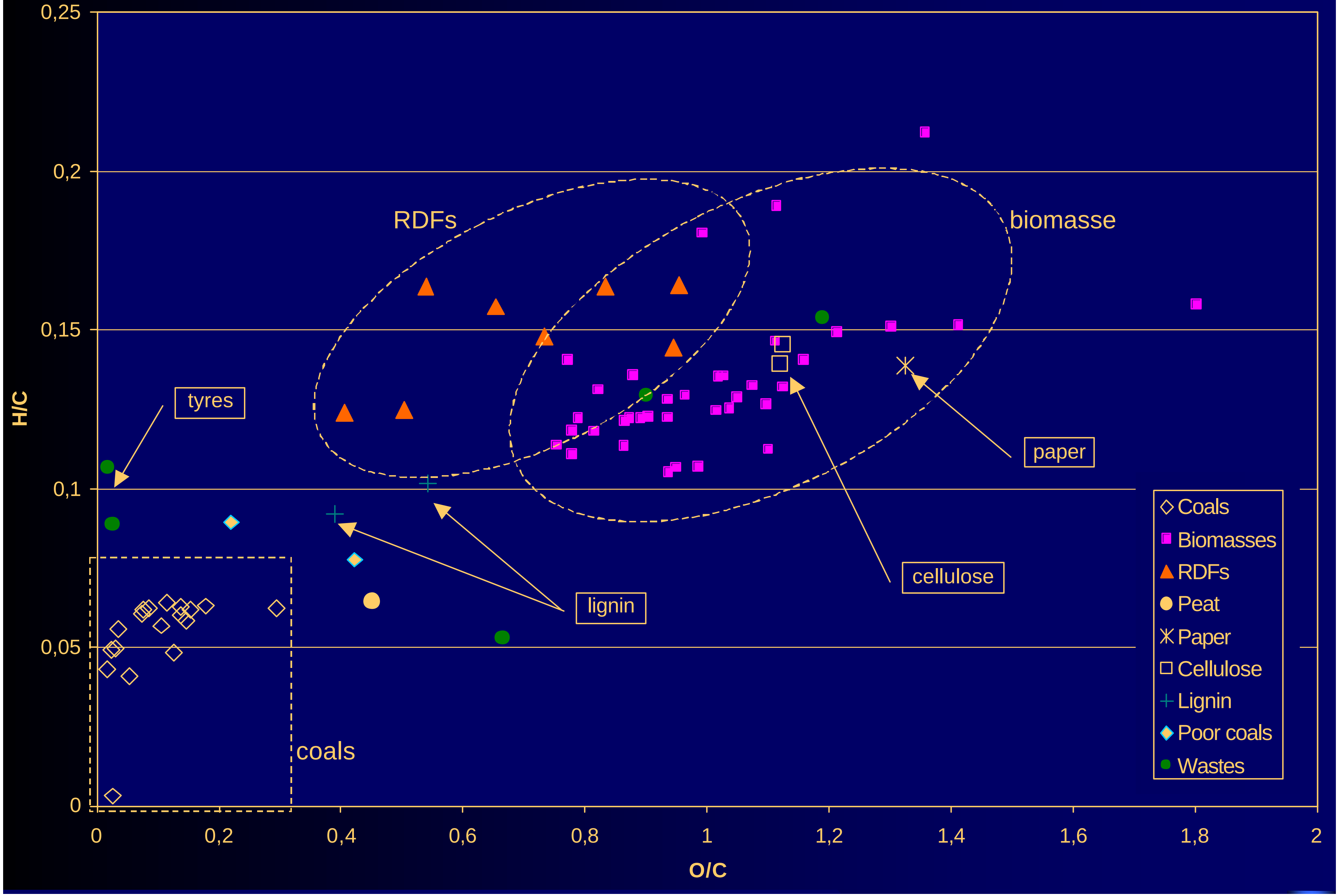
Objectives

Secondary fuel (biomasses, wastes, residues, battle coals, …)

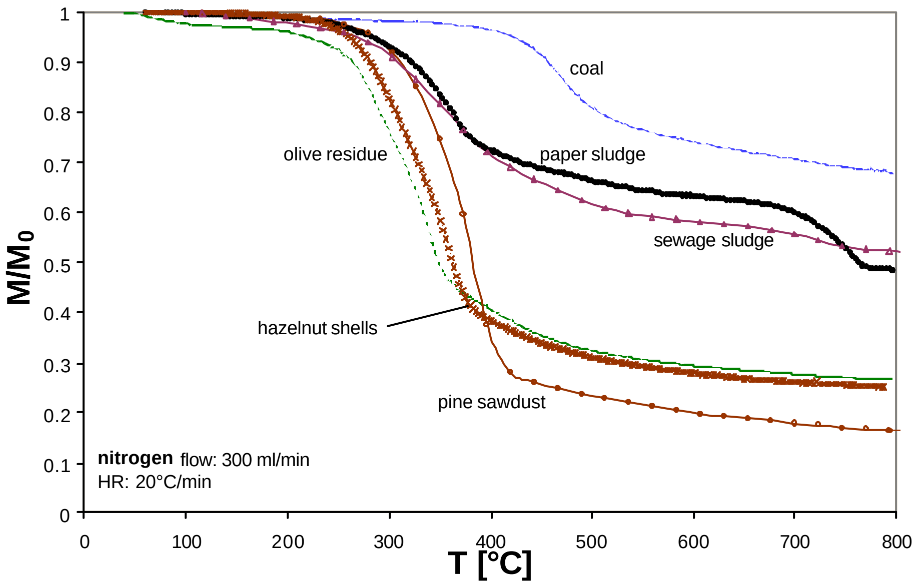
- **Secondary fuels sources**
- **Preparation of sec. fuels (grinding behaviour)**
- **Pre-treatments of sec. fuels**
- **Devolatilization/Pyrolysis of sec. fuels**
- **Ignition and flame development**
- **Oxidation of chars from sec. fuels**
- **Size and structural variations**
- **Reactor fluidynamic**
- **Slagging and fouling**
- **Formation of pollutant species**
- **Modelling of main phenomena**

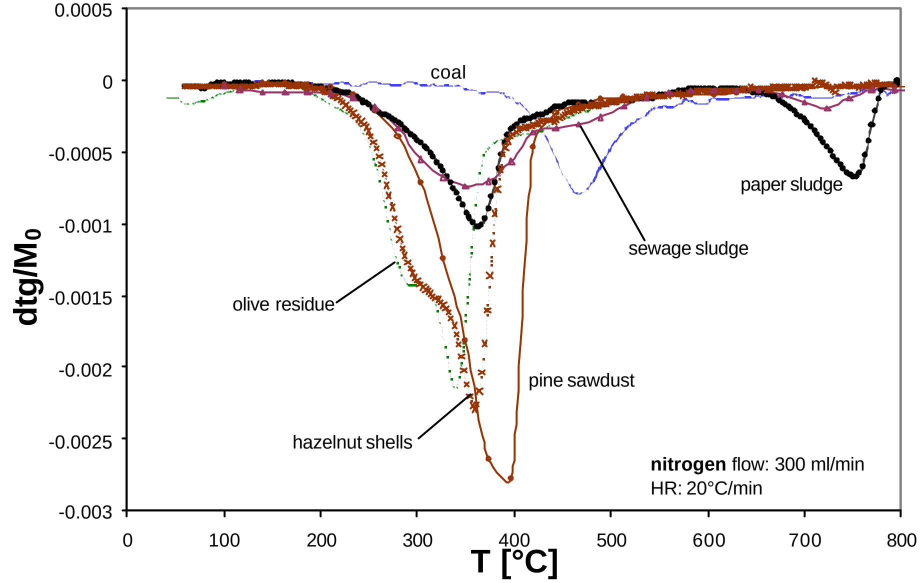


Biomass properties



Biomass properties





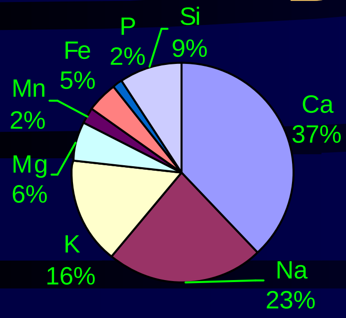
		olive residue	pine sawdust	hazelnut shells	paper sludge	sewage sludge	coal Kema04
Ultimate analysis (dry)	C	51.24	53	51.0	24.27	52	71.43
	H	6.69	6	5.40	3.42	8	4.47
	N	0.83	0.2	1.30	0.51	6	1.12
	S	0.05	0.08	-	0.014	1.2	0.81
	Cl	0.071	0.02	-	0.053	0.5	0.265
Proximate analysis (as received)	Moist.	14.03	(dry)	7.0	54.8	(dry)	5.68
	VM	67.37	80.6	73.0	22.58	47.8	28.73
	FC	17.55	17.7	18.8	1.36	6.6	52.6
	Ash	1.05	1.7	1.2	21.26	45.6	13
LHV (MJ/kg) (dry basis)		20.1	18.1	-	5.14	11.0	28.7

Biomass properties

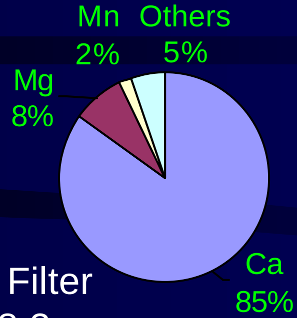
Estimated heating contribution from volatiles

Fuel	HV of volatiles (kJ/kg VM)	VM[a] (%)	Heat from VM (%)	Heat from char (%)
Coal	31,375	36.8	36.3	63.6
Sawdust	17,994	84.5	75.5	24.5
Manure	18,256	82.8	73.3	26.7
Rice husk	15,945	78.8	64.5	35.5
Fuel wood	14,773	79.5	64.2	35.8
Tires	42,360	69.8	75.0	25.0

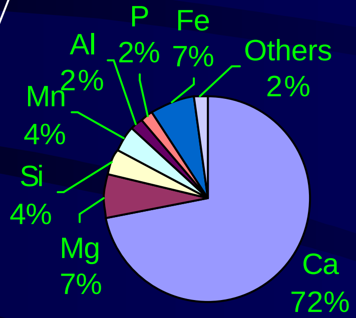
Biomass properties



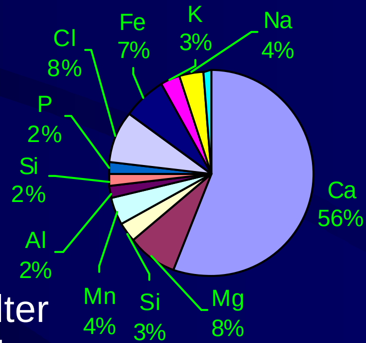
Ash composition of the biomass material (sawdust) fed to the drop tube



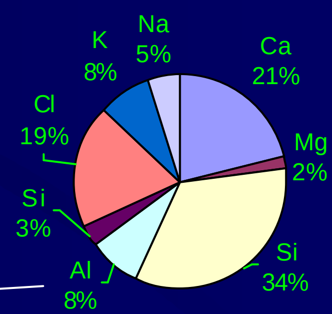
Filter 8.3 μm



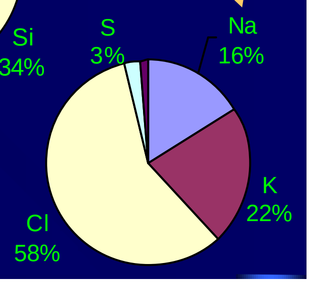
Filter 1.6 μm



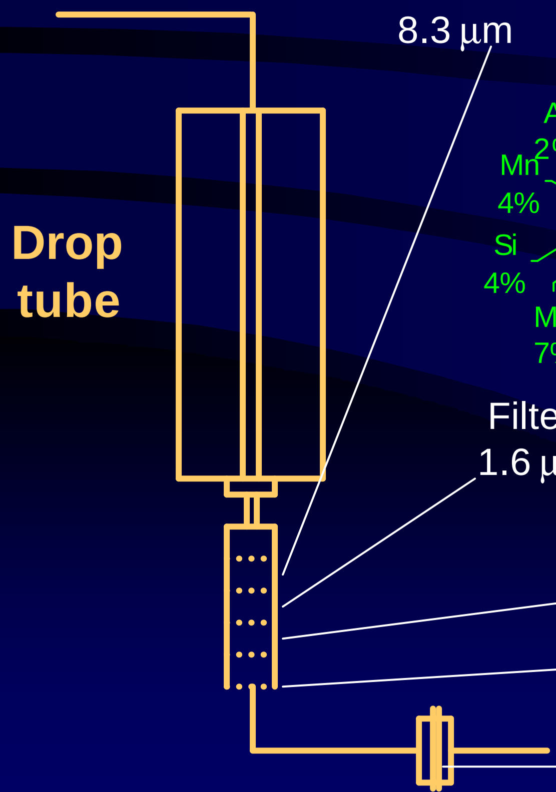
Filter 0.4 μm



Ultimate filter



Aerosol filter



Biomass ash composition

wt% (ash)	miscan-thus	olive	almond shells	poplar wood	oak wood	wheat straw
CO2	1.5	0	0	0	0	5.1
SO3	3.7	2.4	0	0	2.2	4
Cl	1.5	0	0	0	0	3.7
P2O5	1.8	2.7	9.8	0	7.5	4.7
SiO2	63	23.1	12.2	0	2.3	30.6
Fe2O3	0.4	5.1	3.6	0.3	0.5	0.4
Al2O3	0.4	5.3	2.7	0.5	0.9	0.5
CaO	7.1	10.9	17	29.2	65	7.9
MgO	2.8	3	6.5	0.1	8.3	2.4
Na2O	0.2	29.9	2.1	0.4	0.8	0.7
K2O	14.8	5.2	23.4	10.7	9.9	25.3

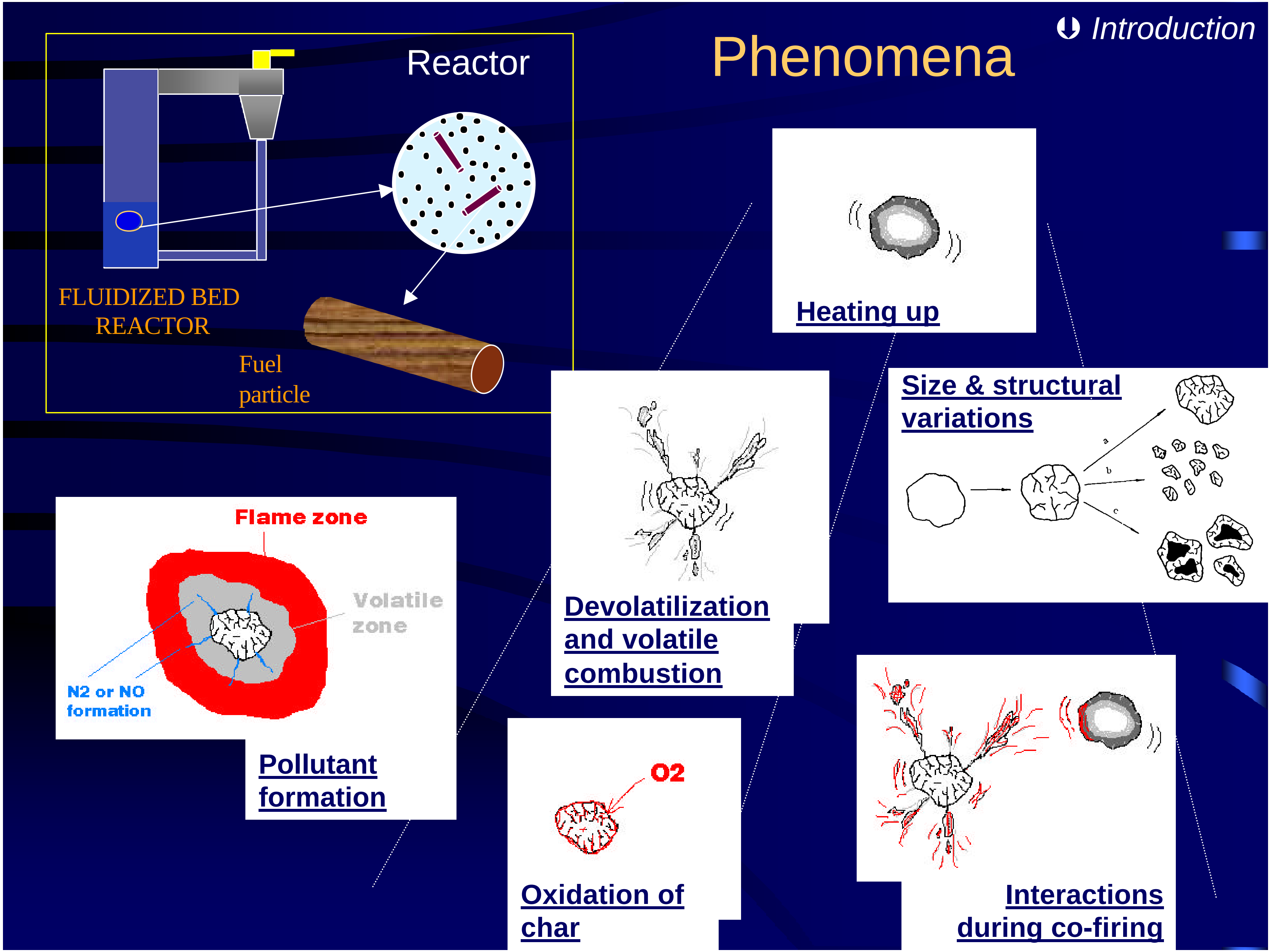
The size of particles collected decreases - increases the concentration of **alkali compounds**

Biomass properties

Comparison of coal and biomass characteristics

- Devolatilization for biomass fuels starts at lower temperature compared to coals
- Volatile content of biomass is higher compared to coal
- The specific heating value of biomass fuels (and also of volatiles released) is lower compared to coal
- Biomass char contains more oxygen than coal
- Biomass fuels contain less sulphur than coals generally employed
- Biomass ashes are more alkaline in nature compared to those of coals

Phenomena


Reactor
FLUIDIZED BED
REACTOR
Fuel
particle
Heating up
Size & structural
variations
a
b
c
Devolatilization
and volatile
combustion
Flame zone
Volatile
zone
N2 or NO
formation
Pollutant
formation
O2
Oxidation of
char
Interactions
during co-firing

Co-Firing aspects

Coal/Biomass blend

- Heating value
- Volatile content
- Reactivity
- Oxygen demand
- Emissions

HV > 20 MJ/kg ⇨ auto-thermal combustion

VM > 35% ⇨ stable flame

Ignition

- Heat release at lower temperature
- Selective oxygen consumption

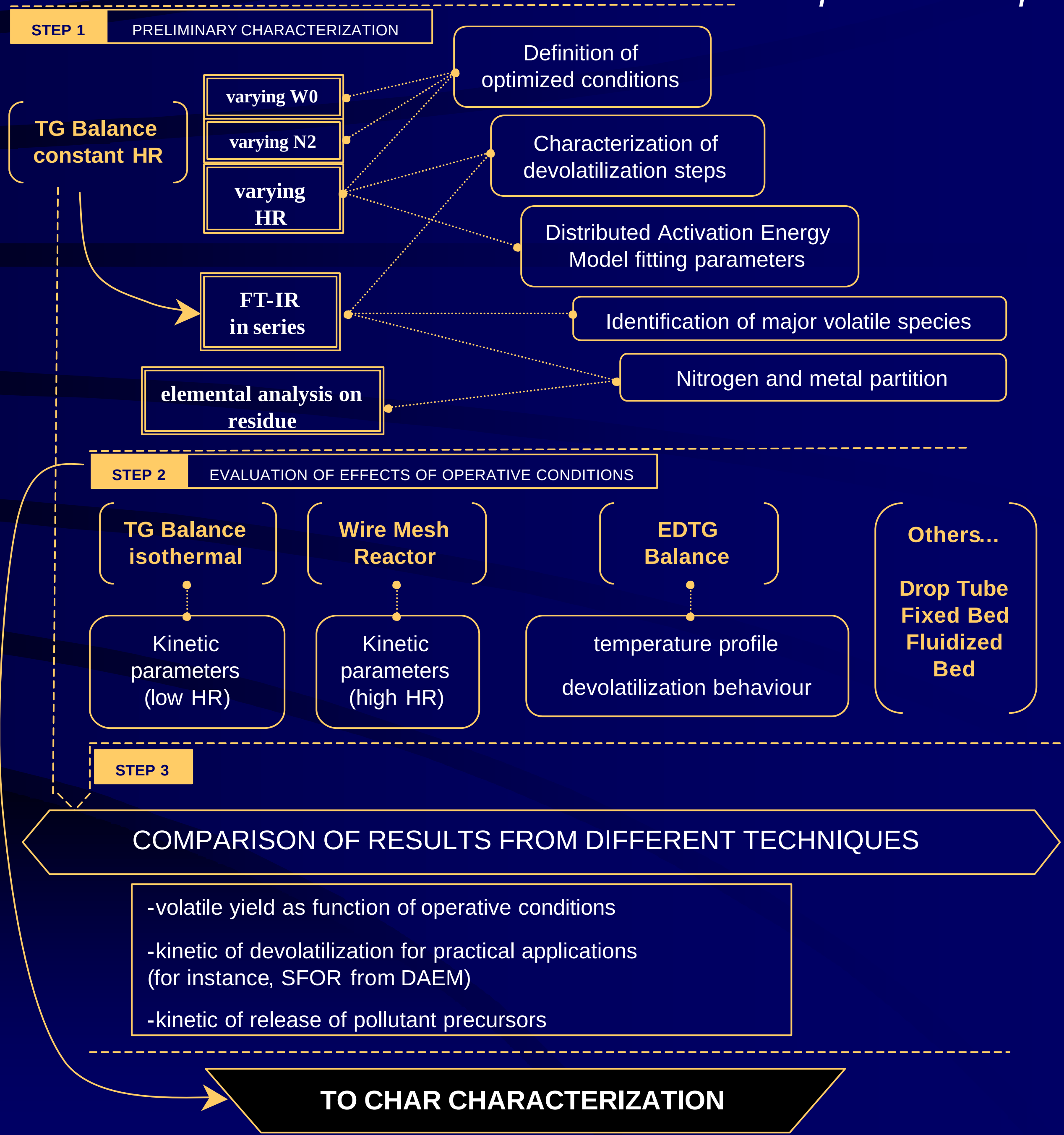
Higher VM content ⇨ higher residence time in reductive conditions ⇨ N_2 formation favoured compared to NO

Characterization of secondary fuels fro co-combustion purposes

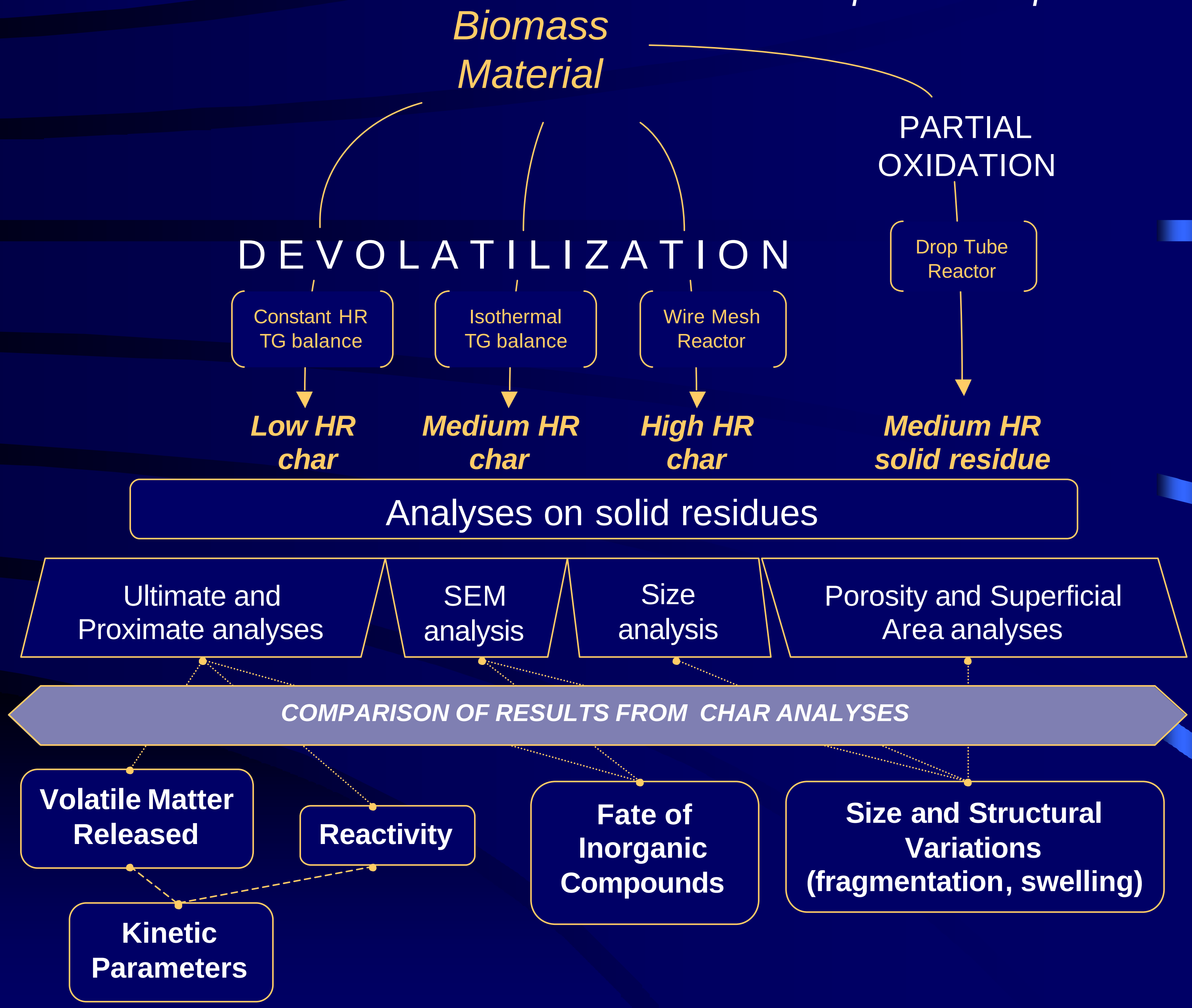
- **Characterization of devolatilization and oxidation of *secondary fuels* in different conditions (temperature, heating rate, reaction environment) and experimental techniques is needed to provide fundamental data for the optimization of operating parameters and fuel properties for combustion systems.**
- **Define procedures for characterisation**
  - **characterisation: the use of different experimental techniques and data abstraction procedures to obtain kinetic data and expressions (sub-models) suitable for describing secondary fuel behaviour.**
- **A modellistic approach to the major phenomena allows various fuels behaviour to be predicted in different operative conditions, in order to optimize the parameters for industrial purpose. The presented models are suitable either for a detailed study on fuels pyrolysis, or to generate specific parameters to be used in comprehensive codes (CFD).**

Experimental Procedure for the Devolatilization of Secondary Fuels

Experimental procedure



Experimental Procedure for the Characterization of Chars from Secondary Fuels



Equipment

Thermogravimetric balance (Mettler TA-3000)

allows to characterize the material as for (constant heating rate runs):

- devolatilization behaviour
- combustion behaviour
- combustion behaviour of char

allows to obtain kinetic parameters (isothermal runs)

Wire mesh reactor (Pyroprobe 1000/2000 CDS)

allows rapid heating (up to 2×10^4 °C/s) and high final temperature (1400°C)

allows to obtain kinetic parameters for operative conditions more similar to the conditions usually encountered in power plants

Drop Tube Reactor

allows to simulate a pulverised fuel reactor in conditions similar to those encountered in practical plants

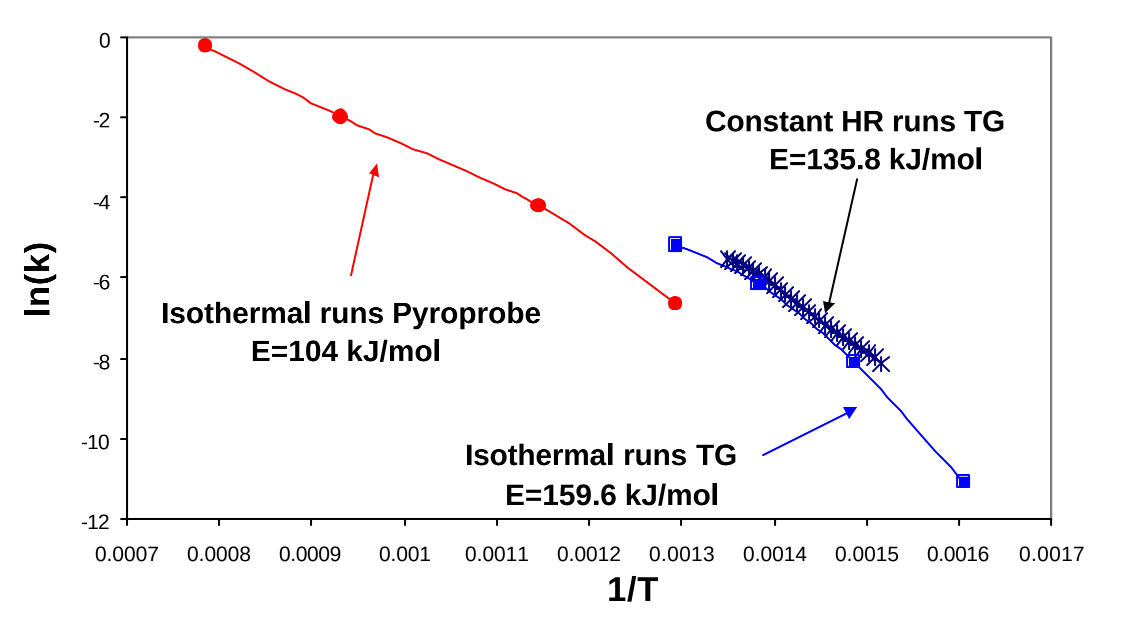
	TG (constant HR)	TG (isothermal)	Pyroprobe	Drop Tube Reactor
T max (°C)	900	600	1400	1200
HR max (°C/s) nominal value	0.5	-	2×10^4	-
HR max (°C/s) evaluated on sample	0.5	50-100	2×10^3	500-1000
residence time (s)	(…)	(…)	0-200	0.5-1.5
sample mass (mg)	5-10	5-10	3-5	stream of particles
gas environment	N_2	N_2	N_2	O_2/N_2

Comparison between TG and Pyroprobe runs

Comparison of volatile matter released from tg balance and pyroprobe:

the higher the heating rate the higher the volatile matter released

Volatile content	TG runs			PYROPROBE runs	
	5°C/min	10°C/min	20°C/min	1000°C	1400°C
Coal			32.4	27.1	35.4
Coal/wood (10%)	31.5		33.3	29.3	37.6
Coal/cacao (10%)			36.4	27.6	36
Olive residue		70.8	71.2	72.7	77.8
Paper sludge	49.8		51	57.3	62.8

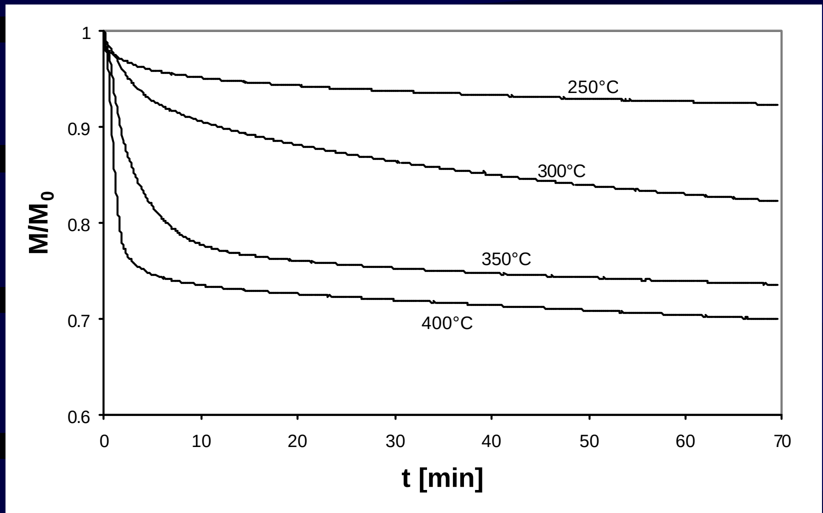


Comparison of kinetic parameters abstracted using different experimenatl techniques for **coal Kema04**

Isothermal runs

Experimental section

TG balance

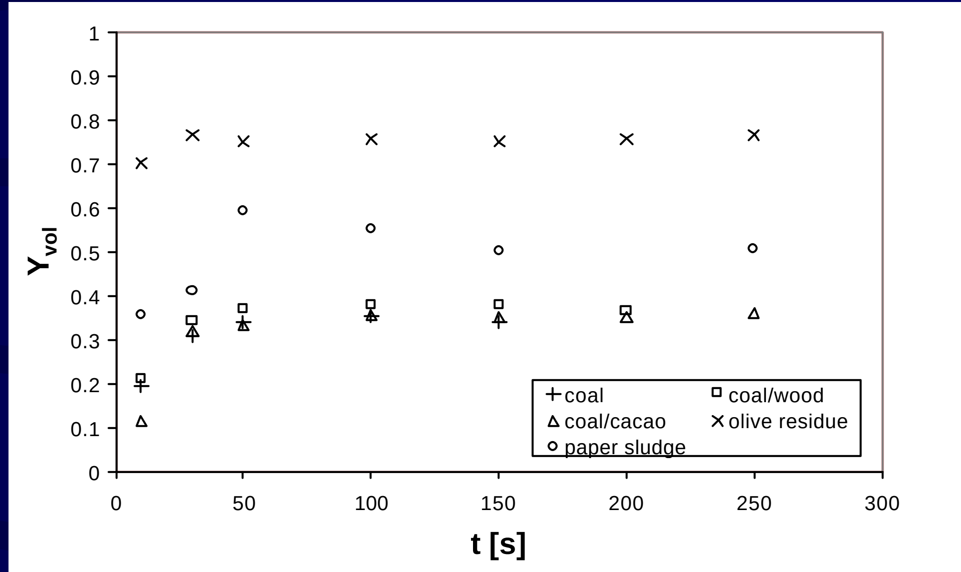


Isothermal runs in TG for **paper sludge** (nitrogen flowrate 300 ml/min M_0 5-10 mg)

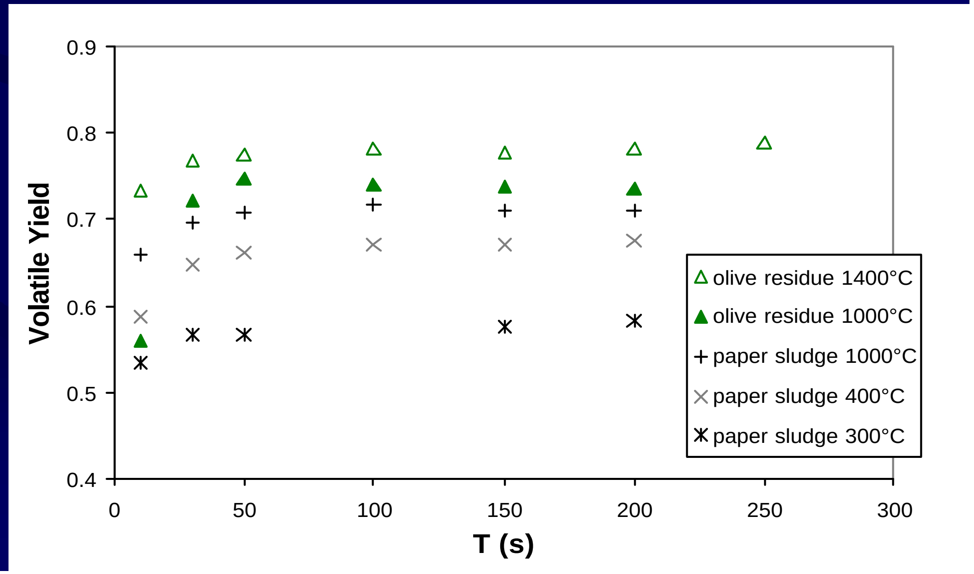
KINETIC PARAMETERS (as function of HR)

Devolatilization of **biomasses (olive residue and paper sludge)** at different residence times and final temperatures in **Pyroprobe** (HR_n=20000°C/s M_0~3 mg)

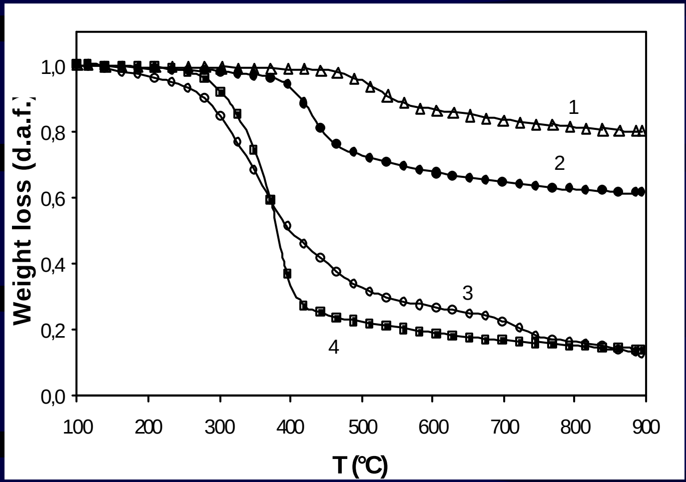
Pyroprobe



Devolatilization of materials at different residence times (T_{fin}=1400°C HR_n=20000°C/s M_0~3 mg)

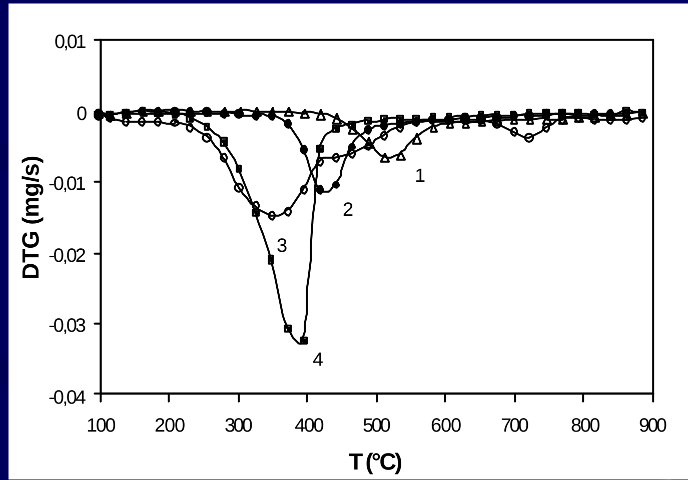


Co-Devolatilization results

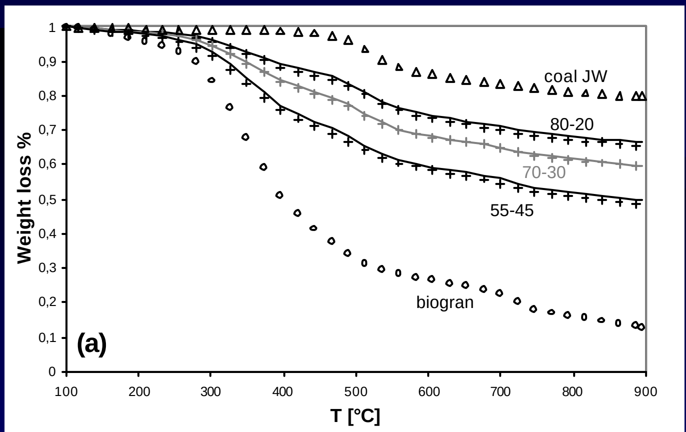


TG devolatilization curves for reference materials*:

(1) coal JW
(2) coal US
(3) sewage sludge
(4) pine sawdust



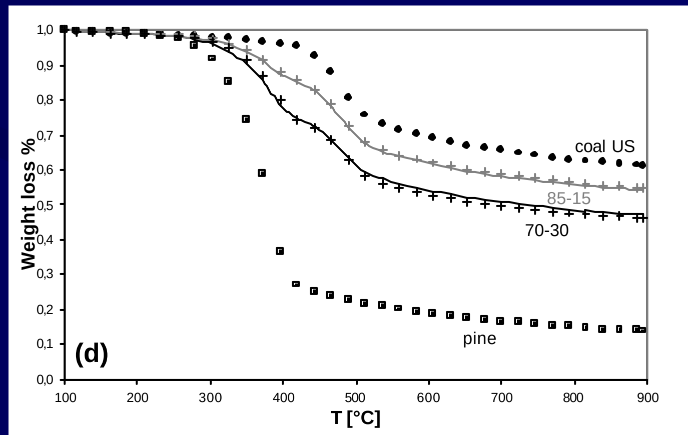
No interaction between biomass and coal during blend devolatilization (though different VM content, reactivity and volatile composition)



TG devolatilization curves for some blends*:

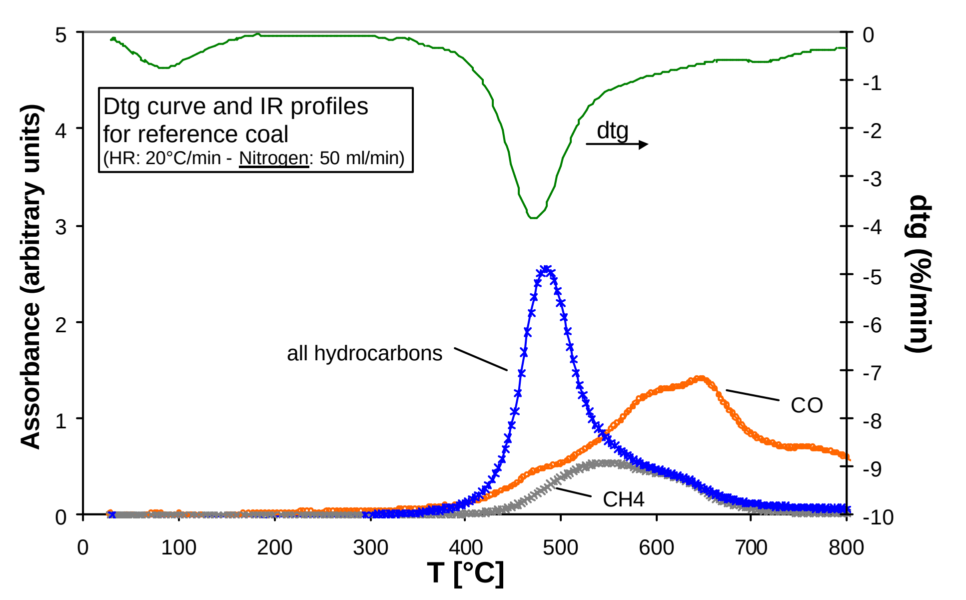
⇦ biogran/coal JW

pine/coal US ⇨



*Operative conditions for all runs: HR 20°C/min - nitrogen flowrate 300 ml/min - M_0 ~10 mg

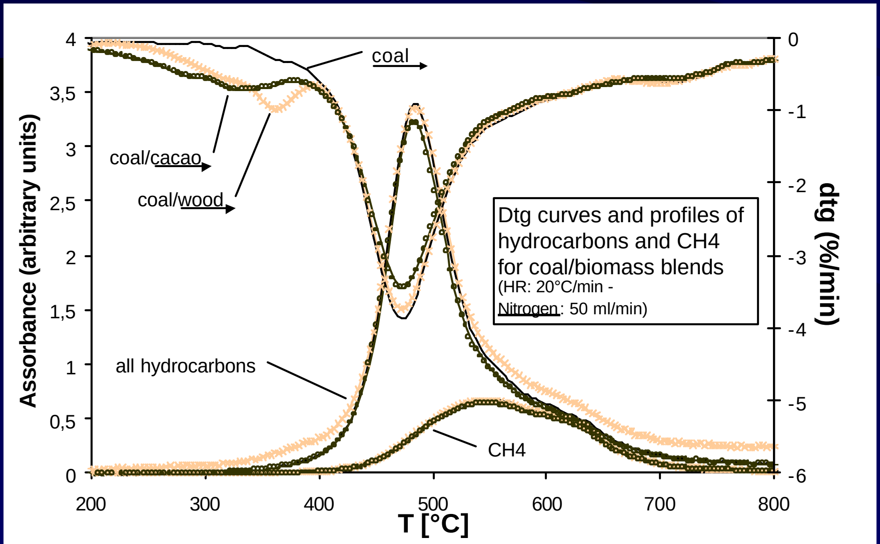
Devolatilization: TG / FT-IR

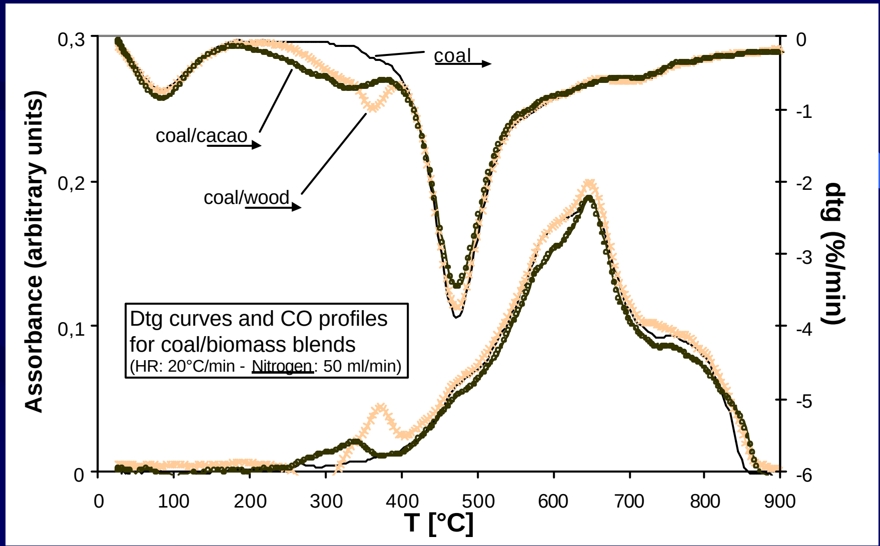


TG/FTIR in series:

- TG/DSC Netzsch STA 409 C (Heating Rate 20°C/min, 40-1000°C, N_2 flowrate 50 ml/min)
- IR spectrometer Bruker Equinox 55

➲ Dtg curve and FT-IR profiles for **reference coal** (operative conditions as reported - M_0~20 mg) and
➲ comparison of **coal/biomass blends**

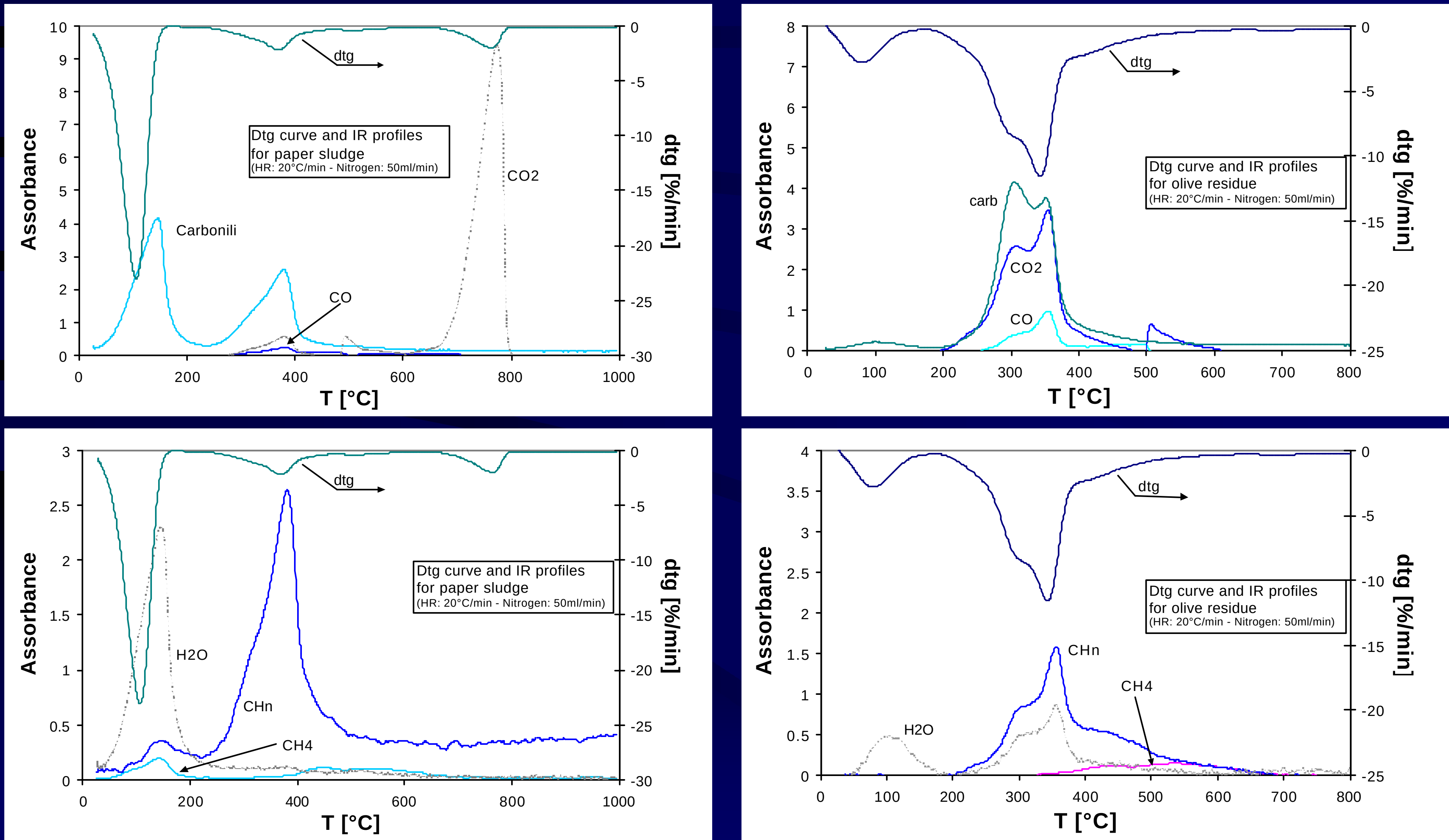




Devolatilization: TG / FT-IR

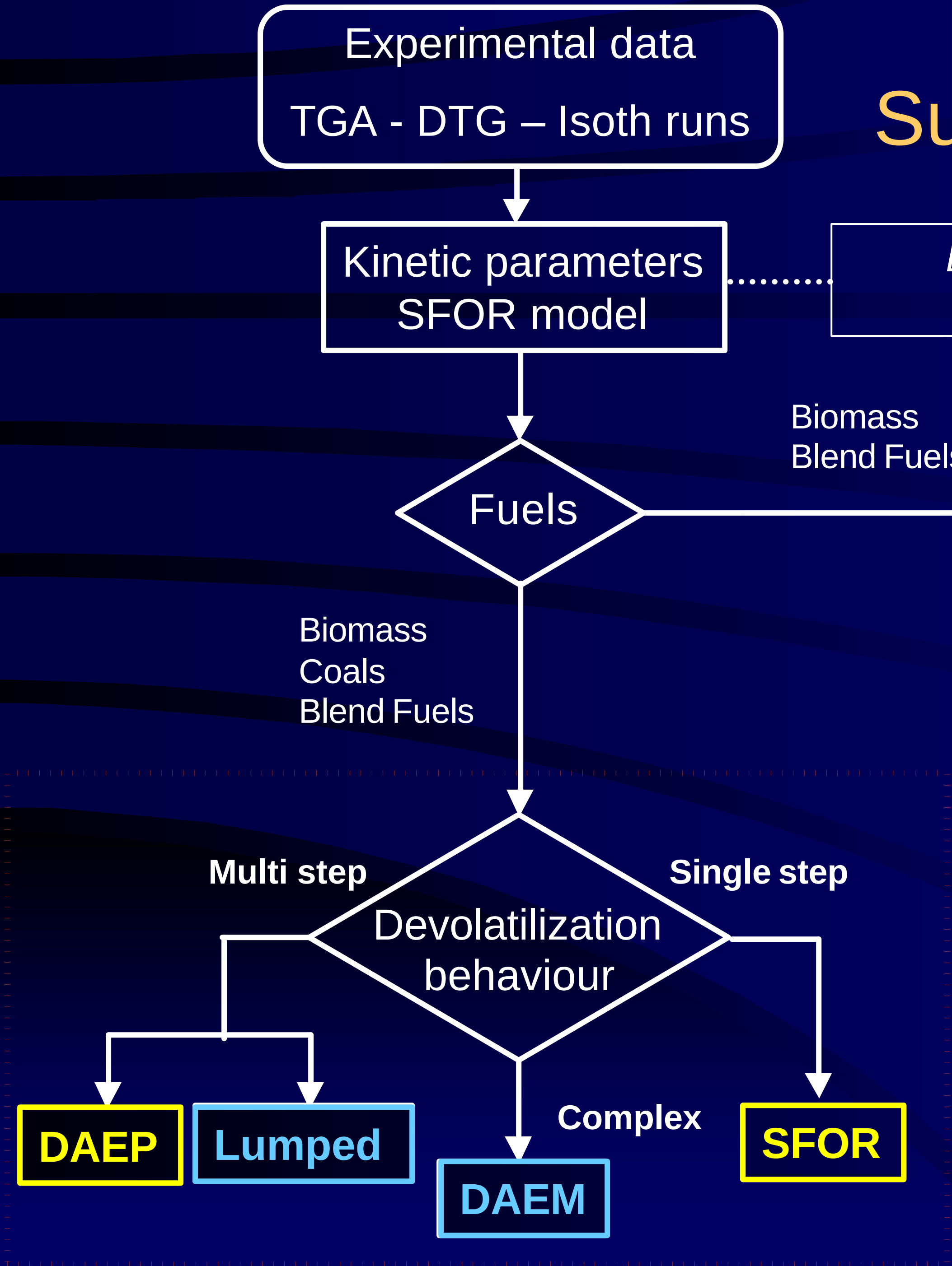
Dtg curve and FT-IR profiles for some biomass fuels

paper sludge and **olive residue**



Modelling

Sub-Modelling Devo



Directly implemented with CFD

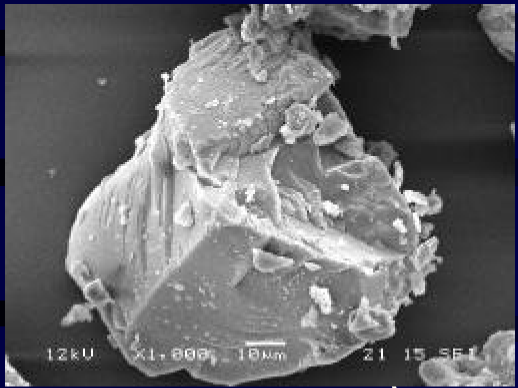
Provide optimized parameters (off-line use)

Modelling-Devo: overview

	Model	Parameters	Properties needed	Balances	Applicability	Characteristics
Devolatilization models	**SFOR**: Single First Order Reaction	2 parameters (A, E)	V^{∞} thermal history	Mass (kinetic)	All materials	Simple scheme Low comp. cost
	DAEP: (n SFOR models)	n*2 (A,E)	Chemical composition n*(V^{∞})	Mass (kinetic)	Blends, composite materials and multi-stage devolatilization	Simple scheme Low comp. cost
	DAEM: Distribution Activation Energy Model	3 parameters (A, E_0, σ)	V^{∞} thermal history	Mass (kinetic)	All materials especially coals	Simple scheme Medium comp. cost
	Lumped: (SFOR+DAEM)	2+3 parameters	Chemical composition V_1^{∞} and V_2^{∞} thermal history	Mass (kinetic)	Blends, composite materials and multi-stage devolatilization	Simple scheme Medium comp. cost
	Neural Network model	Minimization of error function on output values	Physical and chemical properties of sample Chemical composition	No balance	Biomass materials	Black box scheme Very low comp. cost
	CHL model	No fitting parameters	Chemical composition Chem/Phys Properties Operating conditions	Mass and Energy	Biomass Material	Complex model High comp. cost

SEM analysis on solid residue in different conditions

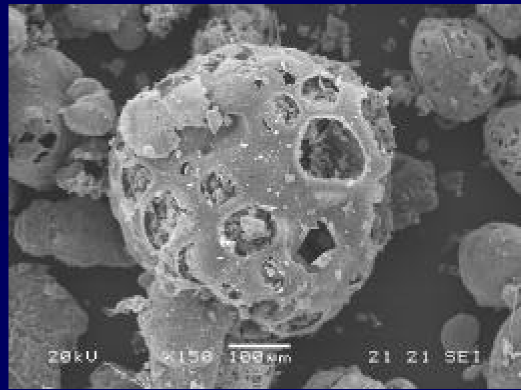
Experimental section



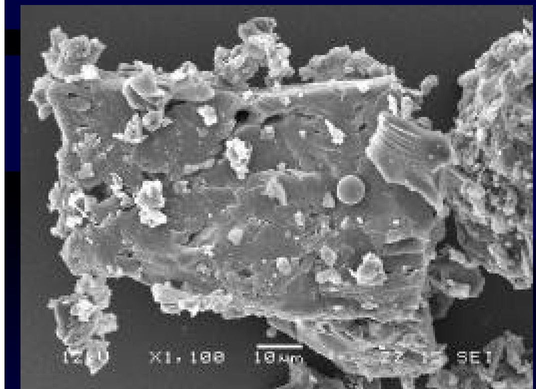
COAL KEMA04 (10wt%) as received

IMAGING

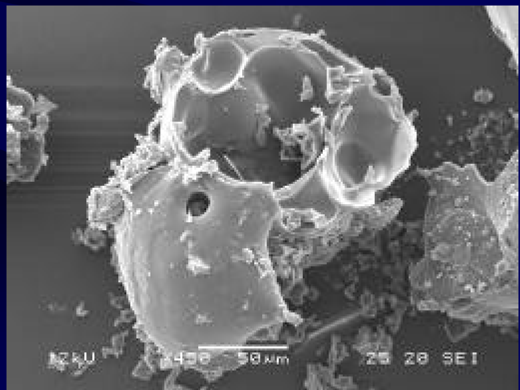
Preliminary analysis of materials and solid residues after devolatilization or oxidation at different conditions



Solid residue after **oxidation in drop tube** (T_n 1000°C)



Solid residue after **devolatilzation in tg balance** (T_{fin} 800°C)

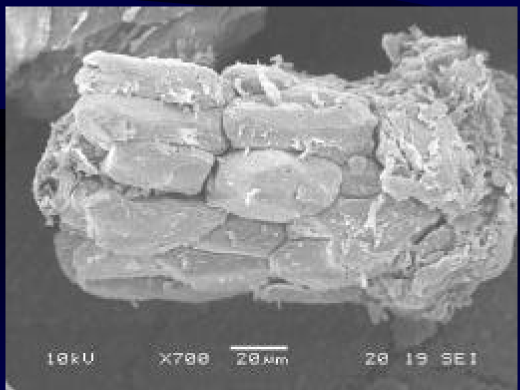


Solid residue after **devo-latilzation in Pyroprobe** (T_{fin} 1400°C)

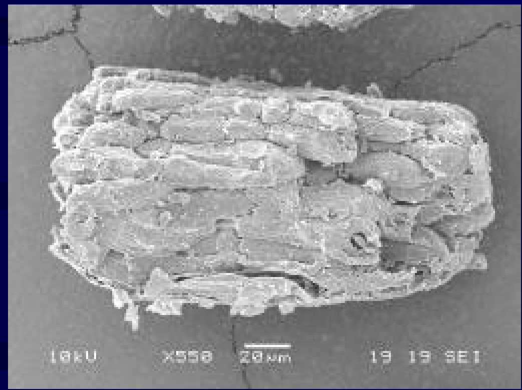
Solid residue after **oxidation in tg balance** (T_{fin} 800°C)

SEM analysis on solid residue

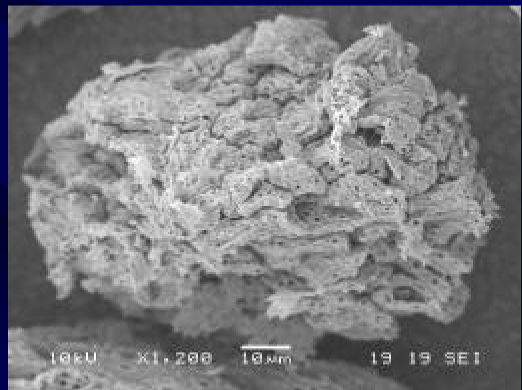
HAZELNUT SHELLS
as received



Solid residue after devolatilzation in TG

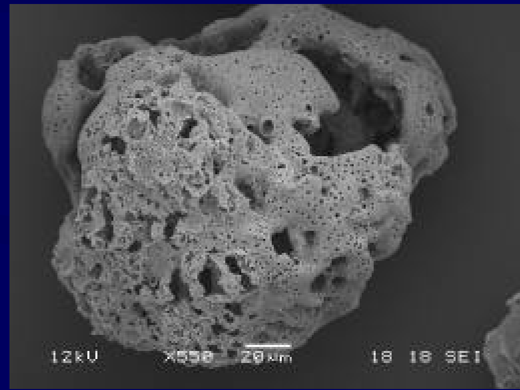


T_{fin} 300°C

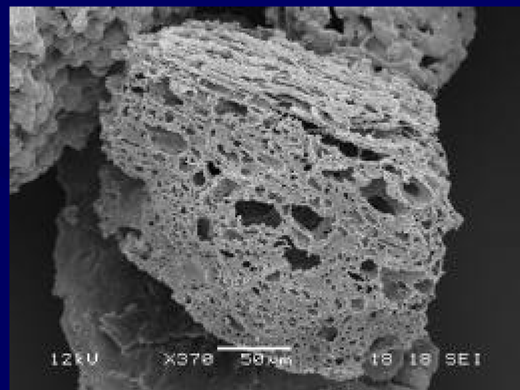


T_{fin} 800°C

Solid residue after partial oxidation in drop tube

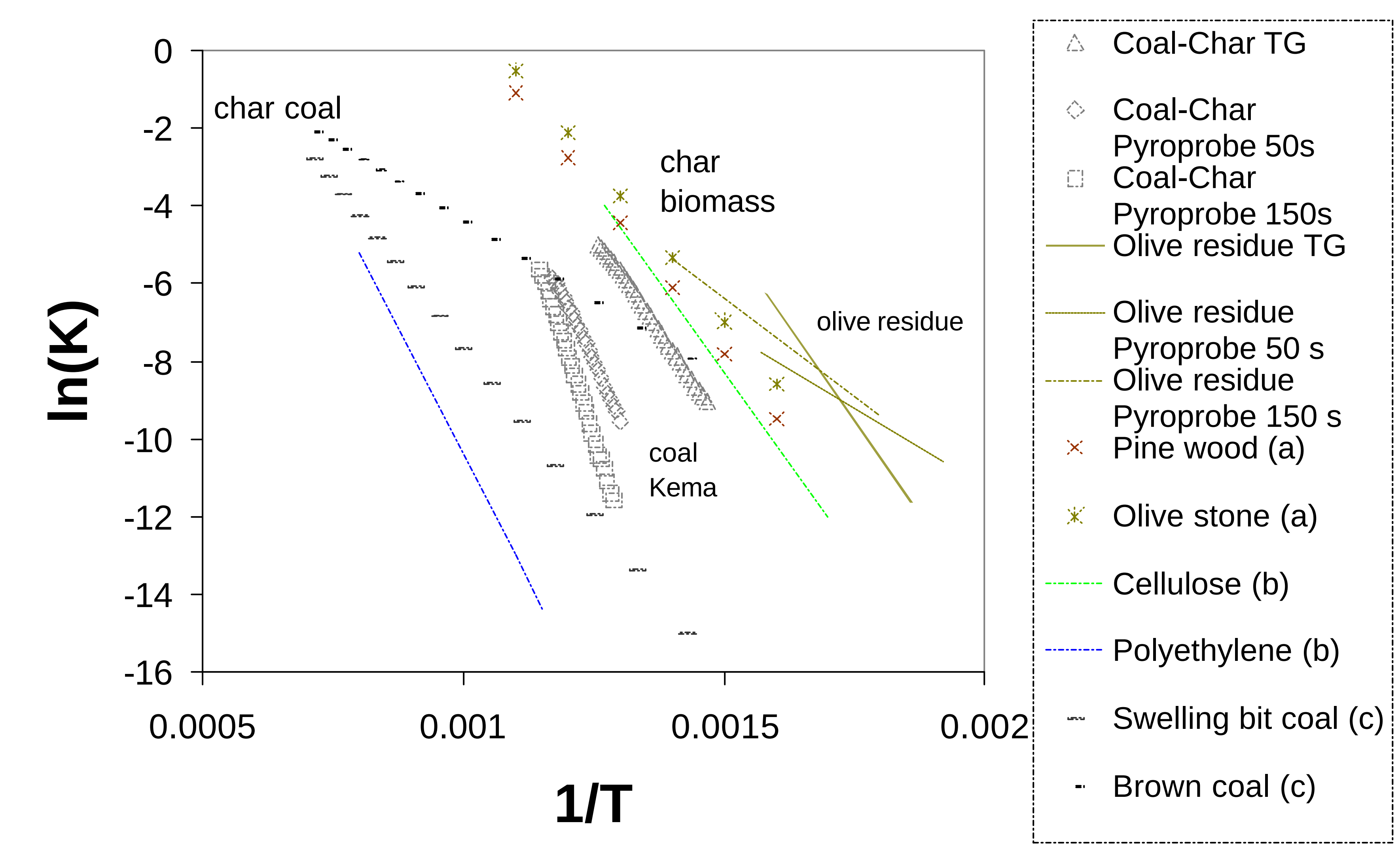


T_n 800°C



T_n 1000°C

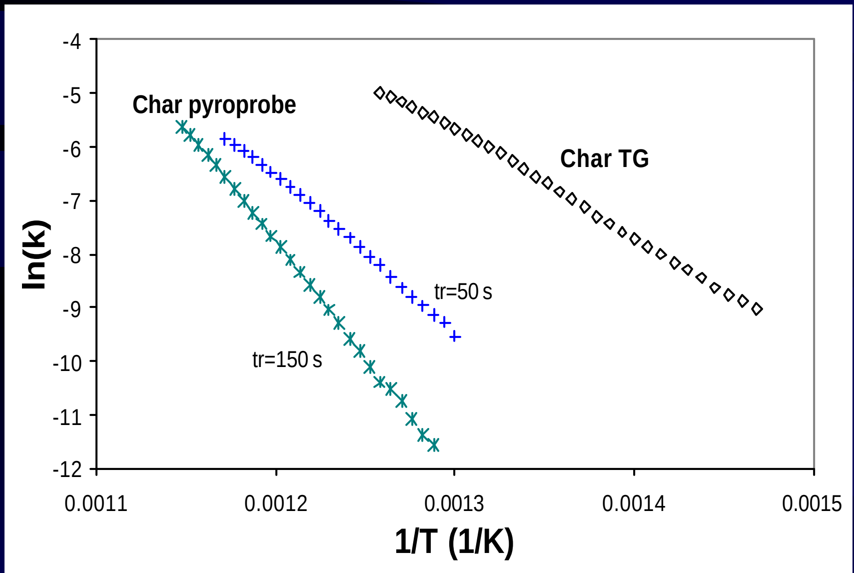
Kinetics of char oxidation



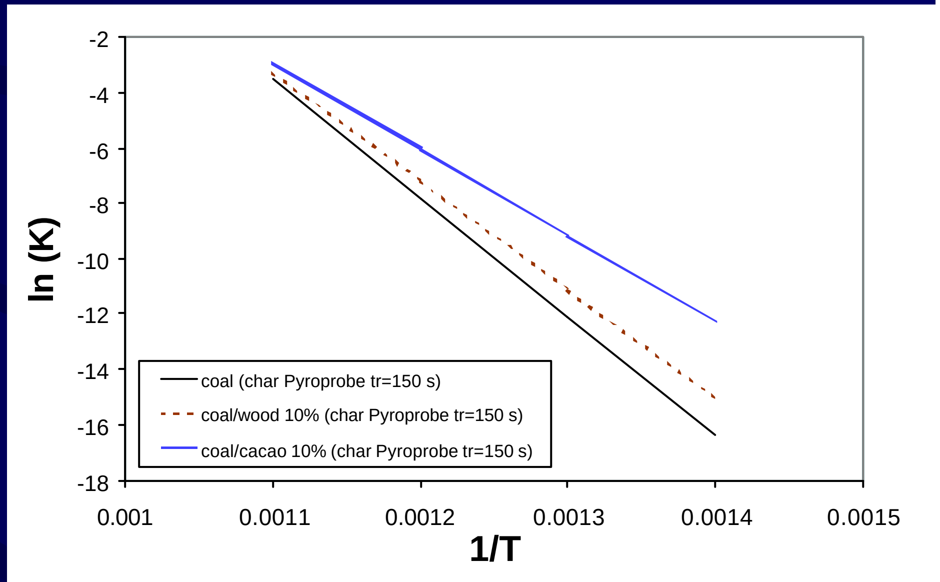
ref (a): J.Adànez, L.F.de Diego, F.Garcia-Labiano: Ind.Eng.Chem.Res. 40, pp.4317-4323 (2001)
ref (b): G.Tatti: Thesis – Dept Chemical Engineering – Pisa (2001)
ref (c): Smith: 19th Symp.(Int.) Combustion (1982)

Kinetics of char oxidation

	Char TG (HR=20°C/min, T_{fin}=800°C)		**Char Pyroprobe** (HR=20°C/ms, T_{fin}=1400°C tr=50s)		**Char Pyroprobe** (HR=20°C/ms, T_{fin}=1400°C tr=150s)	
	E_{att} (kJ/mol)	A (s^{-1})	E_{att} (kJ/mol)	A (s^{-1})	E_{att} (kJ/mol)	A (s^{-1})
coal Kema	166	5.91×10^{8}	241	1.86×10^{12}	357	9.78×10^{18}
coal/wood 10%wt	-	-	201	7.91×10^{9}	327	2.33×10^{17}
coal/cacao 10%wt	-	-	197	1.06×10^{10}	260	4.72×10^{13}
olive residue	158	2.04×10^{10}	67.1	136	84.1	6700
paper sludge	…		…		…	



Arrhenius Plot for coal Kema



Arrhenius plot for char from coal Kema and chars from blends coal/biomass

Co-combustion modelling: steps

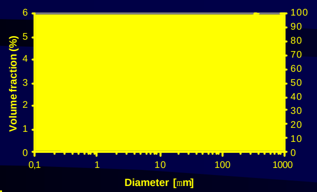
- **Material composition and initial size distribution**

INPUT:
·Ultimate and proximate analysis

Fuel 1

C, H, O, N

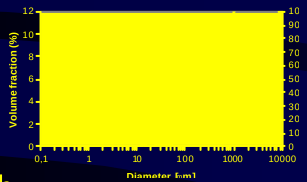
VM, FC, ash



Fuel 2

C, H, O, N

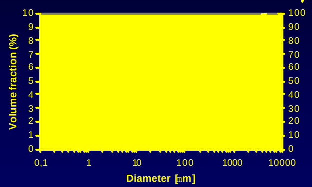
VM, FC, ash



Fuel n

C, H, O, N

VM, FC, ash



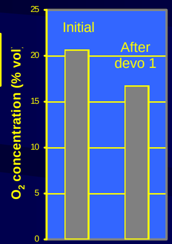
- **Devolatilization & homogeneous combustion step**

INPUT:
·Volatile composition
·Oxygen consumption

Volatile 1

CxHyOz

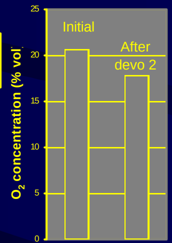
O_2 demand



Volatile 2

CxHyOz

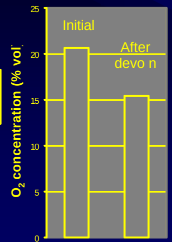
O_2 demand



Volatile n

CxHyOz

O_2 demand



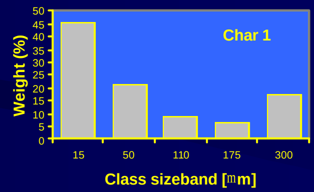
- **Char oxidation**

INPUT:
·Kinetic parameters (exp. or NN generated)
·Size distribution

Char 1

A_1, E_1, n_1

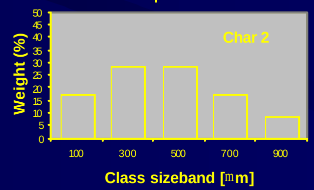
ash content



Char 2

A_2, E_2, n_2

ash content



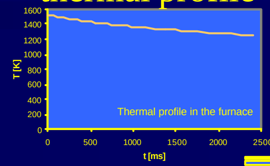
Char n

A_n, E_n, n_n

ash content

INPUT:

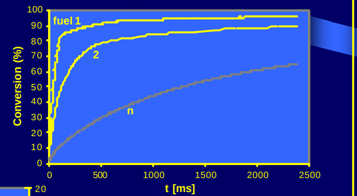
·Experimental thermal profile

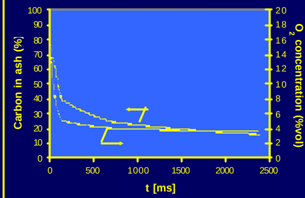


·Evaluated residence time (PFR model)

SIMULATION OUTPUT

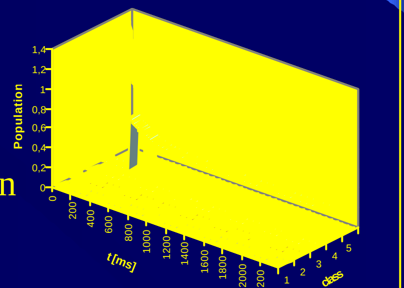
Þ Fuel conversion profile



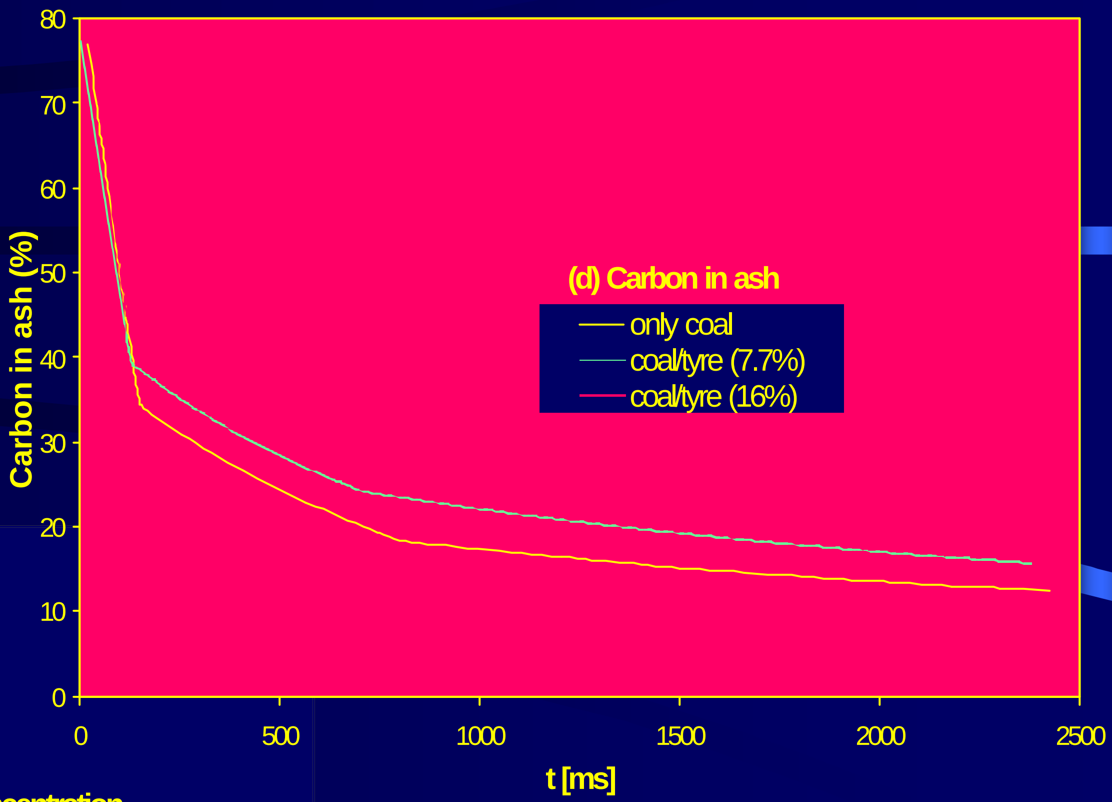


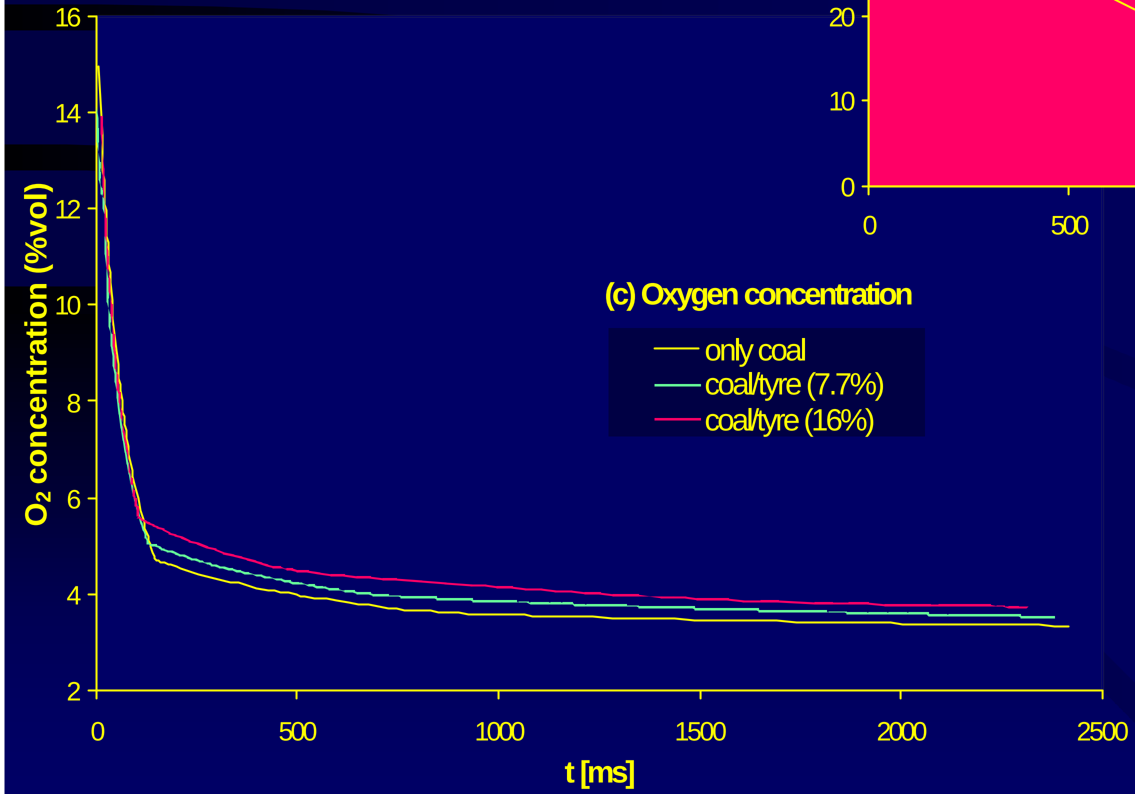
Þ Oxygen concentration and carbon in ash

Þ Size reduction during combustion of char n

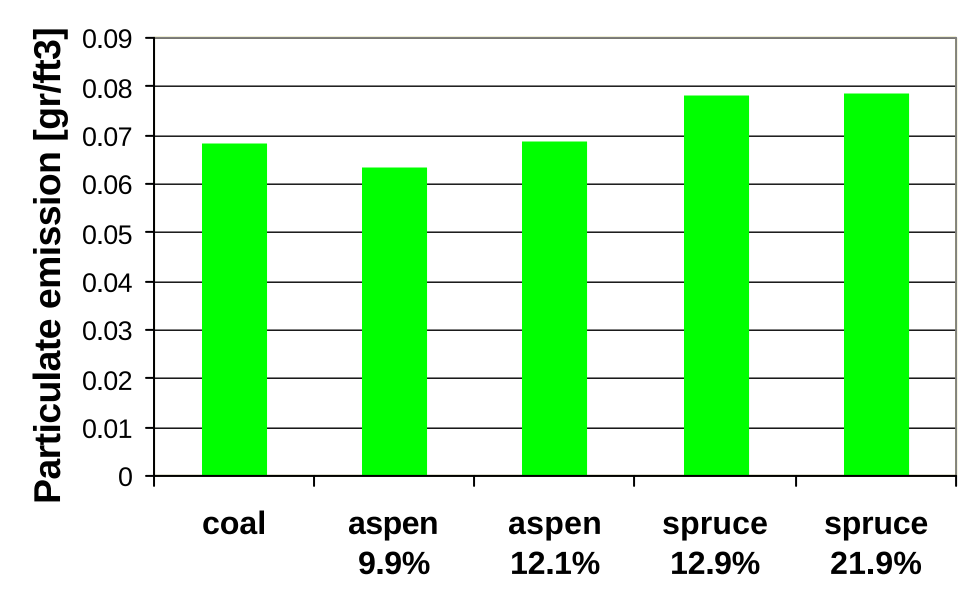


Model results

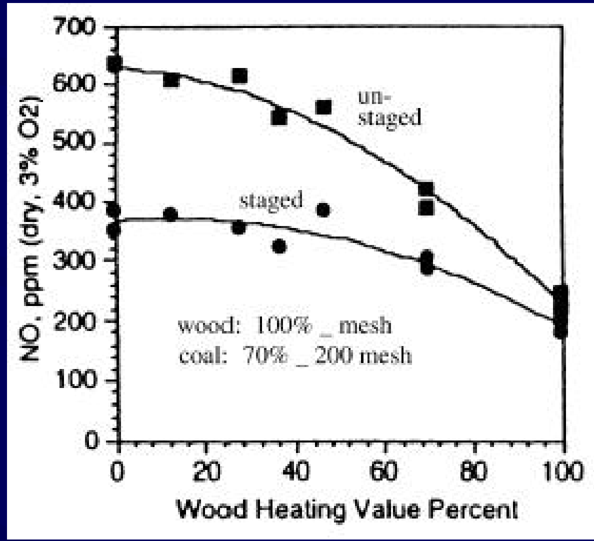




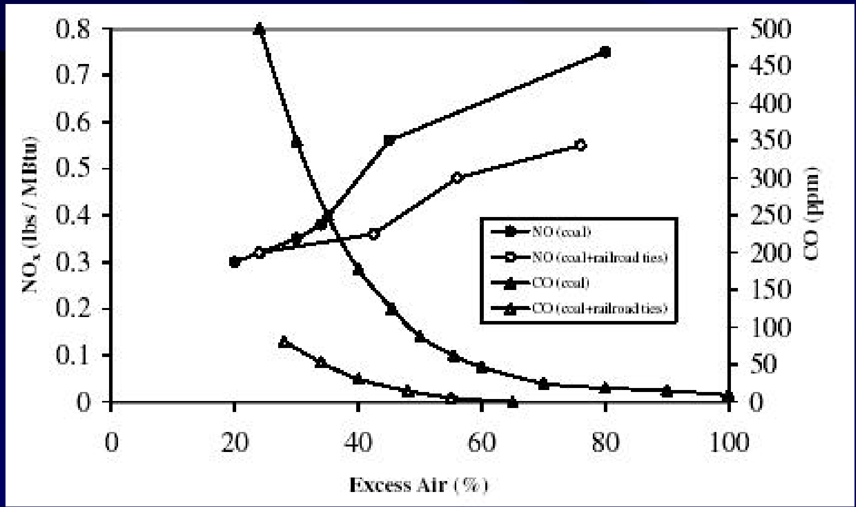
Emissions from co-firing



- **particulate emissions** from the co-combustion of biomass/coal blends



- **NO emissions** as function of wood in the blend (heat basis)



- Effects of co-firing 20% (mass basis) railroad ties with coal on **NO and CO emissions**

Conclusions

- **Biomass properties have been compared to coal properties, remarking positive and negative aspects and the advantages of their use in co-combustion processes**
- **The experimental investigation on co-firing should be referred to the following steps:**
  - **fuels characterization**
    - **devolatilization**
    - **char oxidation**
    - **fate of mineral matter and precursors**
  - **co-devolatilization (experimentally verified that there are no interactive effect during the co-devolatilization of different fuels in blends).**
  - **effects on ignition- flame stability in burners: pilot and full scale trials needed**
  - **co-firing of char obtained from parent materials (especially in conditions similar to practical uses, i.e. high temperature and heating rate)**
  - **pollutant formation (obtaining a correlation usable to predict the emission from co-firing starting from the emission of single fuels)**

Conclusions (2)

- **Modelling**
  - The developed sub-models should be applied to the complex behaviour of the biomass fuels.
  - These sub-models should be used to describe the behaviour of fuels blends considering the interactions during the process (co-pyrolysis, co-combustion…)
  - These models could be used to:
    - provide optimized parameters for industrial applications.
    - implement comprehensive code to simulate the real combustion process.

Co-Firing Modelling

- **Scope**: to describe the burnout and size distribution changes of each fuel char during co-combustion, taking into account the different reactivity, volatile matter content and thus different and competitive oxygen demand.

- No energy balance has been considered, therefore the temperature profile as to be known from the experimental runs (not a restriction because the model should be actually introduced as a sub-model in a more comprehensive model)

- **Hypotheses:**

  Devolatilization is instantaneous: the calculation starts after the flame zone. The total amount of VM should be known (experimentally and/or by specific modelling): needed to calculate the oxygen consumption in the first part of the furnace (flame zone).

Modelling (2)

- Each char behaves independently from the others (to predict char oxidation phase only, and not flame characteristics, which are strongly affected by co-operative influence of parent fuels).
- The characteristics of the char formed in severe conditions have to be known *a priori,* by means of suitable characterisation of char samples.
- Each fuel char may present a different size distribution, since the model can consider the dependence of reactivity on particle size.
- The population for each char and each size class is continuously computed at each calculation step, as well as the oxygen concentration (different chars consume oxygen according to their reactivity).

Modelling

- The population for each char and each size class is continuously computed at each calculation step, as well as the oxygen concentration (different chars consume oxygen according to their reactivity).
- Kinetic parameters for high severity chars: extrapolating low temperature oxidation kinetic data to high temperature, high heating rate conditions.
- The parameters adopted yield a coal char reactivity between 4÷5 times larger than tyre char in the temperature range of interest

	A [kg/m ^{2}s(atm)^n]	E [kcal/mol]	n
coal	703	21.5	1.0
tyre	70	19.7	0.5

Model development

Fuel i ⇨ C(char) + VM (devolatilization step)

VM + O_2 ⇨ CO + H_2O (oxidation of volatiles)

fC(char) + O_2 ⇨ 2(f-1)CO + (2-f)CO_2 (char oxidation)

CO + ½O_2 ⇨ CO_2 (complete oxidation in the gas phase)

(reaction rate on the surface)
$$R_c = k_c A_p C_{O_2,p}$$

(kinetic constant)
$$k_c = A \cdot e^{-\frac{E}{RT}}$$

(oxygen diffusion rate)
$$R_D = k_D A_p (C_{O_2,\infty} - C_{O_2,p})$$

(diffusion constant)
$$k_D = \frac{Sh \cdot d_p}{D}$$

(reaction rate)
$$R = A_p \cdot k \cdot P^n_{O_2,\infty}$$

(effective kinetic constant)
$$k = \left(\frac{1}{k_c} + \frac{1}{k_D}\right)^{-1}$$

(size variation during combustion)
$$d_p = d_0 (1-u)^{1/3}$$

Results

Residence time: assuming a plug flow reactor model with the experimental thermal profile. In all cases, the residence time was about 2500 ms, starting from the section immediately downstream the flame, where char oxidation starts.

Temperature as well as CO and O_2 concentration measurements were performed along the furnace to evaluate the starting point for char oxidation calculation.

Run	model results	experimental	Deviation
1. coal			
final oxygen concentration (% vol)	3.32	3.39	-2.06
final carbon in ash content (% wt)	12.92	13.92	-7.18
2. coal/tyre (7.7%)			
final oxygen concentration (% vol)	3.52	3.43	+2.62
final carbon in ash content (% wt)	15.70	14.48	+8.43
3. coal/tyre (16%)			
final oxygen concentration (% vol)	3.61	4.02	-10.2
final carbon in ash content (% wt)	17.10	18.74	-8.75

Model results